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J.P. Cohen-Addad, M. Domard, G. Lorentz, J. Herz. Polymeric gels. NMR study of elementary chain swelling. Effect of trapped topological constraints. *Journal de Physique*, 1984, 45 (3), pp.575-586. 10.1051/jphys:01984004503057500 . jpa-00209788

HAL Id: jpa-00209788

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Classification

Physics Abstracts

61.40K — 76.60E

Polymeric gels. NMR study of elementary chain swelling. Effect of trapped topological constraints

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(Reçu le 19 juillet 1983, révisé le 2 octobre, accepté le 17 octobre 1983)

Résumé. — L'objectif de ce travail est d'étudier le gonflement progressif de trois gels covalents, de polydiméthylsiloxane, synthétisés à des concentrations, v_c , différentes ; deux bons solvants (chloroforme et heptane) et un solvant-thêta (bromocyclohexane) étaient utilisés comme agents de gonflement.

i) Le gonflement observé à l'échelle macroscopique obéit à une simple loi d'addition des volumes de solvant et de polymère.

ii) La relaxation de l'aimantation transversale des protons liés aux chaînes est analysée pour proposer un processus de gonflement progressif des chaînes élémentaires en deux étapes bien séparées ; dans la première ($1 < q < q_d \sim 3$) les chaînes sont progressivement éliminées les unes des autres et remplacées par le solvant ; la vitesse de relaxation δ obéit à une loi de superposition de la forme :

$$\delta/v_c \propto (qv_c^{5/8})^{-0.6 \pm 0.05}$$

dans la deuxième étape ($q_d < q \lesssim 12$), δ obéit à une loi de superposition de la forme :

$$\delta \propto q^{2/3} v_c^{5/3}.$$

Dans l'intervalle $1 < q \leq q_d$, en présence de bon solvant, les chaînes ont des propriétés gaussiennes ; celles-ci sont identifiées par l'utilisation du solvant-thêta ; elles disparaissent progressivement ($q > q_d$) laissant apparaître un effet de volume exclu qui est complet au gonflement maximum. Les lois de superposition sont interprétées à partir d'une formule de base décrivant le transfert de localisation des propriétés RMN d'une échelle locale à une échelle semi-locale.

Abstract. — This work aims at studying the progressive swelling process of three polydimethylsiloxane covalent gels, synthesized at several volume fractions, v_c ; two good solvents (chloroform and heptane) and a theta-solvent (bromocyclohexane) were used as swelling agents.

i) The macroscopic swelling was found to obey a simple addition law of volumes of solvent and polymer.

ii) The transverse magnetic relaxation process of protons linked to PDMS chains is shown to reflect a progressive swelling process of elementary chains occurring according to two well defined steps. The first one ($1 < q < q_d \sim 3$), is a progressive desinterspersion of chains ; monomeric units are replaced by solvent molecules ; the relaxation rate δ was shown to obey a superposition property :

$$\delta/v_c \propto (qv_c^{5/8})^{-0.6 \pm 0.05} ;$$

in the second step ($q_d < q \lesssim 12$), δ was found to obey another superposition property :

$$\delta \propto q^{2/3} v_c^{5/3}.$$

In the swelling ratio range $1 < q \leq q_d$ and in the presence of good solvents, elementary chains have Gaussian properties ; these are conveniently identified using a theta-solvent ; these properties progressively disappear ($q > q_d$) and an excluded volume effect arises ; this is fully observed on gels at equilibrium with a liquid solvent. Superposition properties are interpreted from a basic formula describing the transfer of localization of NMR properties from a local space-scale to a semi-local one.

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1. Introduction.

The progressive swelling mechanism of elementary chains has not been yet given a full quantitative description although the swelling process of most polymeric gels observed in a macroscopic scale has been shown to generally obey a simple addition law of volumes of polymer and solvents [1]. The problem encountered in elaborating a quantitative description of the spread process of elementary chains founded on a specific model arises from the difficulty to investigate experimental properties of gels in a semi-local space-scale. A solution may be brought to this problem by performing neutron scattering experiments on partly deuterated samples [2, 3]. The purpose of the present paper is to show that gel properties may be conveniently investigated at a semi-local space-scale from NMR measurements, without any labelling of polymer chains, using deuterated solvents only. It is now well established that the transverse magnetic relaxation function of nuclei linked to strongly entangled chains is governed by a residual energy of spin-spin interactions reflecting an average orientational order of monomeric units, induced by temporary topological constraints exerted on chains [4-10]. It has been recently shown that this property also applies to methyl protons linked to elementary chains in calibrated polydimethylsiloxane (PDMS) gels where topological constraints are permanent [11-12]. The relaxation rate, δ , of the transverse spin-system response was studied as a function of the swelling ratio q , of the gel; q is defined as the ratio of the volume, V , of the swollen gel over the volume, V_0 , of the dry gel; a schematic behaviour of δ is depicted on figure 1; the dependence of δ upon q was shown to exhibit two well defined swelling ratio ranges which will be hereafter called q_I and q_{II} , respectively.

i) Starting from a dry gel, the spin-spin relaxation rate, δ , is first observed to decrease as the swelling ratio, q , is increased (q_I range).

ii) Then, δ reaches a minimum value δ_d , corresponding to a swelling ratio q_d .

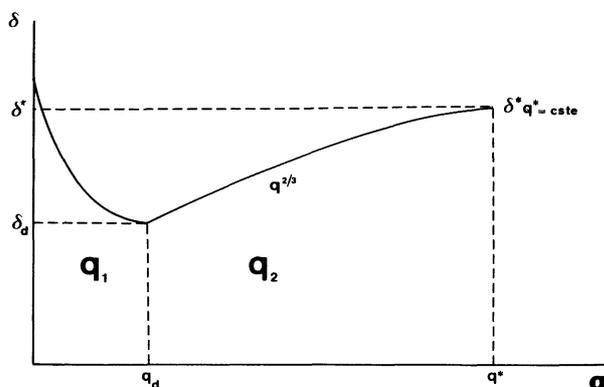


Fig. 1. — The schematic behaviour of the transverse relaxation rate of protons linked to PDMS elementary chains in a gel is described as a function of the swelling ratio, q .

iii) Finally, the most striking and unusual result is the increase of δ observed upon swelling of the gel (q_{II} range); δ was shown to vary according to the following formula :

$$\delta \propto q^{0.67 \pm 0.05} \quad (1)$$

until the value δ^* , corresponding to the maximum swelling ratio, q^* , is reached; δ^* and q^* values were found to obey the approximate relation :

$$\delta^* q^* \simeq \text{constant} \quad (2)$$

for different elementary chain lengths. A schematic swelling process of calibrated gels was proposed in reference [12]; the q_I swelling ratio range was supposed to describe the progressive desinterspersion process of elementary chains, swollen by one another in the dry gel. In the q_{II} swelling ratio range, a packing condition was supposed to govern the spatial organization of elementary chains; this is reflected by formula (1), while formula (2) was derived from the c^* -theorem proposed by de Gennes [13].

The present paper aims at bringing a quantitative support to the foregoing interpretation by extending the previously reported NMR study to calibrated PDMS gels synthesized at several polymer concentrations; furthermore, a theta-solvent will be used in an attempt to identify the q_d swelling ratio with Gaussian properties of elementary chains.

Semi-dilute solutions are known to exhibit hydrodynamic screening effects characterized by a correlation length ξ [13]; this is also considered as the average spacing between topological constraints exerted on entangled chains [14]. Therefore, the average density of topological constraints added to covalent crosslinks in a gel is supposed to be varied by changing the synthesis concentration of the gel [15]. This NMR study will attempt to elucidate the rôle of trapped topological constraints on the swelling mechanism of elementary chains in a gel. It has been already shown from quasi-elastic light scattering measurements that the mesh size of the network is decreased by increasing the concentration of synthesis of the gel; furthermore, the cooperative diffusion constant was found to depend upon this concentration of synthesis according to a scaling law, in agreement with semi-dilute solution properties [16].

Finally, it is worth emphasizing that a transfer of localization of NMR properties from a local space-scale to a semi-local one ($\geq 30 \text{ \AA}$) has been already considered as the basic hypothesis underlying the description of the magnetic relaxation process observed on most slowly fluctuating polymer systems [10]; another purpose of the present work will be to give a quantitative support to this key assumption.

Theoretical aspects concerning the description of NMR properties observed on entangled chains or on crosslinked molecules will be given in section 2. The experimental procedure will be described in

section 3. Macroscopic swelling properties will be reported in section 4 while elementary chain swelling properties observed from NMR measurements will be analysed in section 5.

2. NMR semi-local approach : theoretical aspects.

A quantitative theoretical description of some NMR properties observed on molten polymer systems has been given in reference [10]; the main results of this description will be evoked in this section.

2.1 AVERAGE ORIENTATIONAL ORDER OF MONOMERIC UNITS. — The principle of the NMR observation of gel properties is to monitor the average orientational order of monomeric units necessarily induced by any topological constraint exerted on elementary chains; this average orientational order is measured through the strength of the residual energy of dipolar interactions of nuclear spins located on monomeric units. This property can be analysed in the following way. We consider a given polymer chain segment built from N_e main chains bonds of equal length a ; any temporary non-zero end-to-end vector \mathbf{r}_e of the chain segment gives rise to a reduction of entropy associated with non-isotropic rotations of skeletal bonds : monomeric units are not free to explore all directions in space with a uniform statistical weight. Consequently, a non-zero average of tensorial interactions of spins linked to monomeric units arises from the presence of the topological constraint reflected by the end-to-end vector \mathbf{r}_e . The key formula used in reference [10] to relate the residual energy, $\hbar\varepsilon$, of spin-spin interactions to \mathbf{r}_e and to basic parameters of the chain segment is :

$$\varepsilon(\mathbf{r}_e) = (\Delta_0/a^2) (\mathbf{r}_e/N_e) \begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix} (\mathbf{r}_e/N_e). \quad (3)$$

Formula (3) was calculated by using a model built from a freely jointed chain carrying one proton pair per covalent bond \mathbf{a} ; Δ_0^2 gives an order of magnitude of the second moment of the resonance line which would be observed on the polymer system in the glassy state. Formula (3) is extended to real chains by adjusting the numerical factor Δ_0 but its mathematical structure is not modified; it is not the purpose of the present work to theoretically justify this extended property; this will be gone in a subsequent paper. Formula (3) is qualitatively understood as follows; entropic effects on the residual energy of spin-spin interactions are described by N_e : the larger, the number of bonds, given a end-to-end vector \mathbf{r}_e , the more isotropic, the rotation of skeletal bonds; also, stiffness effects on $\hbar\varepsilon$ are described by averages over \mathbf{r}_e : the lower the stiffness of the chain segment, given a number of bonds N_e , the more isotropic the rotational diffusion of monomeric units. To apply formula (3)

to the interpretation of NMR properties we consider that the detail about rotational isomerization processes may be ignored; also, effects of topological constraints exerted on a given chain segment are supposed to be entirely reflected by a non-zero end-to-end vector whatever the actual complexity of these constraints.

2.2 THE SPIN-SYSTEM RESPONSE. — Formula (3) must be extended not only to real chains but also to real spin-systems. It has been already shown that it applies to the description of NMR properties observed on proton pairs linked to entangled cis-1,4-polybutadiene chains [9]; it also applies to the interpretation of magnetic relaxation properties observed on methyl groups linked to PDMS chains; dipolar interactions of a spin-system arranged in a triangular group have a simple expression when the triangle is equilateral and it is supposed to rotate around its normal [17]; then this expression is easily handled to calculate the spin-system response.

For both a proton pair or a methyl group the residual energy $\hbar\varepsilon$ of spin-spin interactions leads to a transverse magnetic relaxation function $\mathcal{M}_m(t)$, characterized by a pseudo-solid behaviour easily controlled from a spectrum narrowing effect induced by sample rotation [18] :

$$\mathcal{M}_m(t) = \langle \cos(\varepsilon(\mathbf{r}_e) t) \rangle. \quad (4)$$

Two cases must be distinguished from each other to calculate the average value $\langle \rangle$, considering either strongly entangled chains or polymeric gels.

2.3 STRONGLY ENTANGLED CHAINS. — In a strongly entangled polymer chain system, this average is calculated over all end-to-end vectors, considering a Gaussian distribution function; its width is the average distance between entanglement coupling junctions [9, 10]. The second moment, M_2^m , of the resonance line associated with the relaxation function $\mathcal{M}_m(t)$ is known to be given by [20] :

$$M_2^m = - \left(\frac{d^2 \mathcal{M}_m(t)}{dt^2} \right)_{t=0} \quad (5)$$

or

$$M_2^m = \langle \varepsilon(\mathbf{r}_e)^2 \rangle \propto \Delta_0^2 C_\infty^2 / N_e^2 \quad (6)$$

where C_∞ is a measure of the stiffness of the chain [21]; entropic and stiffness effects on the NMR signal clearly appear from formula (6). It is worth emphasizing that the estimated order of magnitude of M_2^m is quite small compared with the second moment Δ_0^2 which would be observed in glassy state; $\sqrt{M_2^m/\Delta_0^2} \simeq 2.5 \times 10^{-2}$ for $C_\infty = 5$ and $N_e = 200$. The deviation of monomeric motion from an isotropic rotational diffusion, induced by topological constraints, is quite a small effects; nevertheless, it is easily observed from high resolution NMR spectroscopy.

2.4 POLYMERIC GELS.

2.4.1 *The packing condition.* — On the other hand, the basic assumption underlying the interpretation of NMR properties observed on polymeric gels in the swelling ratio range, q_{II} , is to consider that the end-to-end vector \mathbf{r}_e is also the vector joining any two covalent crosslinks, neglecting high frequency fluctuations of end-points of elementary chains; the spatial organization of elementary chains is supposed to be governed by a packing condition. Accordingly, the average value $\langle \varepsilon(\mathbf{r}_e) \rangle$ in formula (4) is calculated over all orientations in space of \mathbf{r}_e vectors keeping their mean length equal to :

$$|\mathbf{r}_e| \propto (qN_e)^{1/3}. \quad (7)$$

Therefore, the relaxation rate, δ , of $\mathcal{M}_m(t)$ is expected to vary as :

$$\delta \propto \langle \varepsilon(\mathbf{r}_e) \rangle_{\text{orient.}} \propto q^{2/3}. \quad (8)$$

This dependence has been already observed on several PDMS gels [11, 12]; this observation will be extended to other PDMS gels in the present paper.

2.4.2 *The c^* -theorem.* — Several years ago de Gennes suggested that elementary chains in a polymeric gel in equilibrium with a liquid good solvent should be swollen in the same way as similar no crosslinked chains in a semi-dilute solution considered at the overlap concentration c^* ; one of the ways which can be used to prove that the key formula (3) reasonably applies to the interpretation of NMR properties observed on gels is to consider several polymeric gels characterized by different elementary chain lengths and swollen at equilibrium with a given liquid solvent. Applying the c^* -theorem proposed by de Gennes, the maximum swelling ratio q^* is simply expressed as :

$$q^* \propto (N_e^{3/5})^3 / N_e = N_e^{4/5}, \quad (9)$$

while the residual energy of spin-spin interactions should be expressed from formula (3), (7) and (9) as

$$\delta^* \propto (q^*)^{2/3} / N_e^{4/3} = 1/q^*. \quad (10)$$

Therefore, the relaxation rate, δ^* , of the transverse magnetization observed at equilibrium swelling and the swelling ratio q^* are expected to obey the relation

$$\delta^* q^* = \text{constant}. \quad (11)$$

The above formula does not depend upon elementary chain length. We already called this property the c_v^* -theorem because it is an application of the c^* -theorem [13]; it will be extended to polymeric gels with trapped topological constraints, in the present paper.

2.4.3 *Study of trapped topological constraints.* — One of the purposes of the present paper is an attempt

to elucidate the rôle of trapped topological constraints on the swelling process of elementary chains in a gel. Recently, Candau *et al.* proposed to relate the dynamical modulus G and the cooperative diffusion coefficient D_c measured on polymeric gels synthesized at different polymer concentrations to an average elementary chain length determined by the dynamic screening effect which is known to occur in semi-dilute solutions [14-16]. The interpretation of NMR properties observed on PDMS gels synthesized at different concentrations, v_c , will be found on the same assumption; accordingly, the number of main chain bonds in the elementary chain defined from trapped topological constraints will be supposed to be proportional to $v_c^{-5/4}$, applying recent descriptions of semi-dilute solutions of polymer chains in a good solvent [13]. Therefore the relaxation rate, δ , of the transverse magnetization observed in the q_{II} swelling ratio range should be expected to vary as

$$\delta \propto q^{2/3} / N_e^{4/3} \propto q^{2/3} v_c^{5/3} \quad (12)$$

while the c_v^* -theorem should be illustrated by

$$\delta^* v_c^{-1} = \text{constant} \quad (13)$$

if the maximum swelling ratio q^* and the concentration of synthesis are found to experimentally obey the formula :

$$q^* \propto v_c^{-1}. \quad (14)$$

It will be shown in the next sections that experimental results are in reasonable agreement with formulae (12)-(14); a cut in correlations of space fluctuations of chains is induced by trapped topological constraints as well as by covalent crosslink points.

2.5 SEMI-LOCAL NMR PROPERTIES. — To conclude this section it is worth emphasizing that the key formula (3) actually describes a transfer of localization of NMR properties from a local space-scale (monomeric unit size) to a semi-local scale corresponding to the dynamic screening length or to the distance between end-points of the mean elementary chains (taking trapped topological constraints into consideration) in covalent gels. This space-scale transfer is the specific property which permits to study the slow disentanglement relaxation of long entangled chains or the swelling process of elementary chains from the transverse magnetic relaxation process of nuclei linked to polymer molecules. Also, it is worth noting that formula (3) leads to a study of static gel properties since only time averaged fluctuations at equilibrium are observed from the residual energy of spin-spin interactions. Individual dynamical properties of monomeric units are represented by a uniform average orientational order which is described through a single parameter $\varepsilon(\mathbf{r}_e)$.

3. Experimental.

All PDMS networks were synthesized according to an experimental procedure previously reported, by reacting α - ω , di(hydrogeno) polysiloxane with tetra(allyloxy) ethane [22]. The precursor polymer with hydrogenosilane functions had a molecular weight $M_n \sim 9\,700 \text{ g. mol}^{-1}$. The crosslinking reactions were carried out in the presence of toluene at polymer concentrations equal to 0.84, 0.74 and 0.46, respectively; samples are called H9, H11 and H13, respectively; toluene is a good solvent of PDMS chains.

A dry polymeric gel sample of known weight was immersed in the studied solvent to observe the progressive swelling process. The gel volume was measured by periodically extracting the sample at given time intervals.

Spin-echo measurements were performed using a WP 100 Bruker Spectrometer and a homemade apparatus operating at 32 MHz. Any given swelling ratio was obtained in a sealed NMR sample tube, from the equilibrium of solvent molecules absorbed in a gel with molecules in the solvent vapour [23]; this experimental procedure is much more convenient than the use of several expansive deuterated solvents of various qualities chosen to induce several swelling equilibrium concentrations. Also, a very small swelling ratio lower than that obtained by using any theta-solvent can be obtained by using this experimental procedure.

4. Macroscopic swelling properties.

Before studying the swelling mechanism of elementary chains, it is worth describing the macroscopic swelling of polymeric gels using several good solvents and a theta-solvent.

4.1 GOOD SOLVENTS. — The swelling ratio, q , of the H9 sample ($v_c = 0.84$) was measured as a function of chloroform concentration, from pycnometry; variations of q are reported on figure 2A as a function of the number of solvent molecules n_s per monomeric unit (n_m is the number of monomeric units in the gel). A straight line is observed until the maximum swelling

ratio is reached; the same linear variation is observed on H11 and H13 gel samples using chloroform (Fig. 2A); q is expressed as :

$$q = 1 + \lambda n_s/n_m \quad (15)$$

where λ is necessarily defined as the ratio [12] :

$$\lambda = M_s \rho_p / M_p \rho_s \quad (16)$$

M_s and M_p are the molar weights of a solvent molecule and a monomeric unit, respectively, ρ_s^{-1} and ρ_p^{-1} are the partial specific volumes of the solvent and the polymer, respectively. The value of λ (1.05) calculated from the specific volumes of the pure polymer and pure chloroform is compared with the experimental slope (1.1) in table I. Analogous linear variations are observed from the swelling ratio of H9, H11 and H13 samples using either heptane or toluene (Fig. 2B, 2C). The good agreement between calculated values of λ and experimental slopes (Table I) means that mixing occurs without any appreciable change in the total volume of the system (polymer plus solvent) as it has been assumed by Flory [1]. All measurements were performed at room temperature, 293 K. The progressive macroscopic swelling of the gel was observed as a time function illustrated by figure 3.

4.2 THETA-SOLVENT. — The macroscopic swelling of H9, H11 and H13 gel samples was also observed using bromocyclohexane ($\text{CH}_2(\text{CH}_2)_4\text{CHBr}$) as a theta-solvent; the theta-temperature is known to be about 302 K [24]. Results of measurements are reported on figure 4; the observed linear variation of the swelling ratio is characterized by a slope $\lambda = 1.66$ while the calculated value of λ is 1.60. Therefore, mixing of the gel and the theta-solvent also occurs with a simple addition of volumes when a theta-solvent is used. The volume of the partly swollen gel was measured as a time function illustrated by figure 5.

4.3 TRAPPED TOPOLOGICAL CONSTRAINTS. — Swelling ratio values, q^* , observed after the gels are fully swollen are reported in table II; value of the product $q^* v_c$ are not found to appreciably vary for a given polymeric

Table I. — Macroscopic swelling experimental slopes of figures 2 and 3 are compared with theoretical values.

Solvent	ρ_s g/cm ³	M_s	$\rho_p M_s / \rho_s M_p$	Experimental slope	PDMS without crosslinks
Heptane	0.68	100	1.92	1.9	
Toluene	0.87	92	1.39	1.4	
Chloroform	1.49	119.5	1.05	1.1	1.1
Bromocyclohexane	1.34	163.6	1.60	1.6	

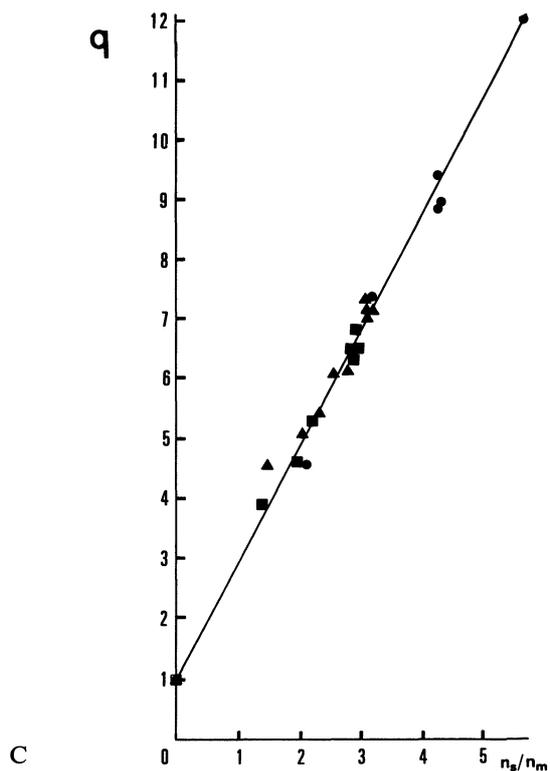
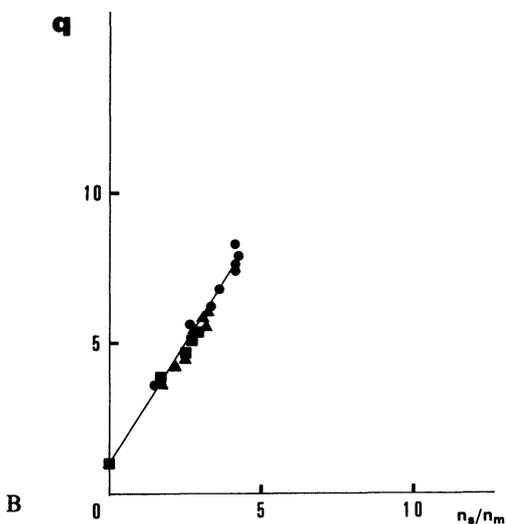
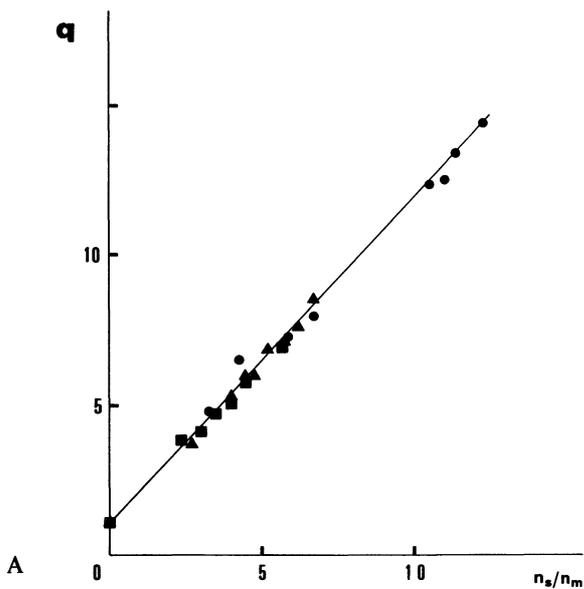


Fig. 2. — Swelling ratio q of PDMS gels observed at room temperature as a function of the number of solvent molecules per monomeric unit n_s/n_m ; ■ H9, $v_c = 0.84$; ▲ H11, $v_c = 0.74$; ● H13, $v_c = 0.46$. The swelling agent is : A : chloroform ; B : heptane ; C = toluene.

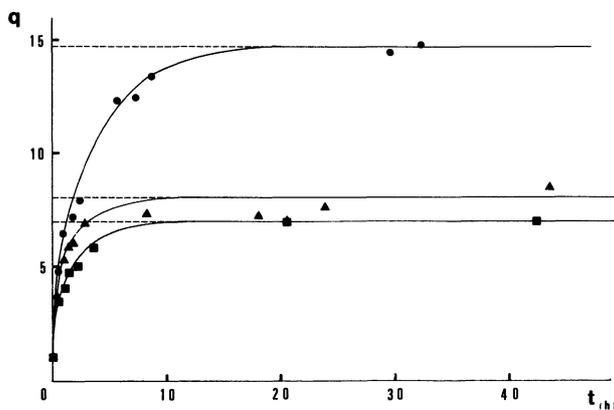


Fig. 3. — Kinetics of swelling of H9, H11 and H13 gel samples; ■ H9, $v_c = 0.84$; ▲ H11, $v_c = 0.74$; ● H13, $v_c = 0.46$. The swelling agent is : chloroform.

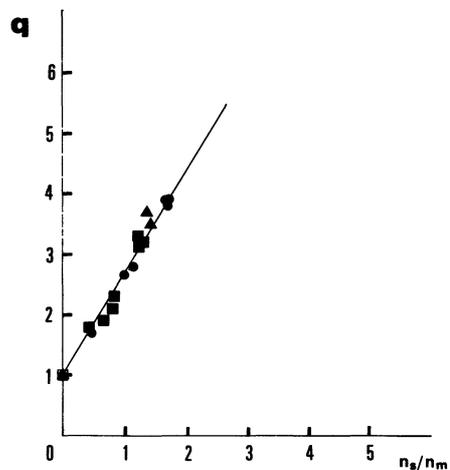


Fig. 4. — Swelling ratio q of PDMS gels observed at 302 K as a function of the number of molecules of a theta-solvent (bromocyclohexane) per monomeric unit n_s/n_m .

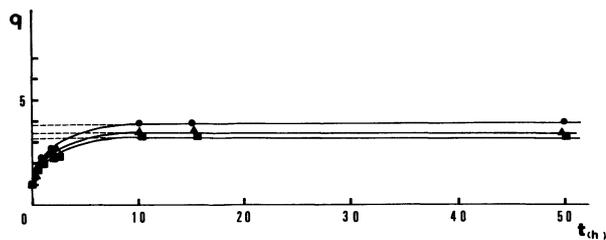


Fig. 5. — Kinetics of swelling of H9, H11 and H13 gel samples. The swelling agent is : bromocyclohexane.

Table II. — Values of the swelling ratio q^* observed on gels at equilibrium with several solvents. Values of the product $q^* v_c$ are also reported.

		$v_c \rightarrow$			
		0.46	0.74	0.84	
$M = 9\ 700$	q^*	14.5	8.0	7.0	} Chloroform
	$q^* \cdot v_c$	6.7	5.9	5.9	
	q^*	12.0	7.4	6.7	} Heptane
	$q^* \cdot v_c$	5.5	5.5	5.6	
	q^*	9.0	6.0	5.4	} Toluene
	$q^* \cdot v_c$	4.1	4.4	4.5	

gel-solvent system, considering several concentrations of synthesis (Table II). Such a result is consistent with both the c^* -theorem proposed by de Gennes and the determination of elementary chain contour length from screening effects related to the concentration of synthesis v_c : $N_e \propto v_c^{-5/4}$ (Fig. 6). The same property applies, considering the swelling equilibrium ratio q_θ^* observed from a theta-solvent ; q_θ^* is expressed as :

$$q_\theta^* \propto N_e^{1/2} \propto v_c^{-5/8} . \quad (17)$$

Variations of q_θ^* observed on H9, H11 and H13 gels are reported as a function of $v_c^{-5/8}$ on figure 7.

5. Elementary chain swelling properties.

In this section, the relaxation process of the transverse magnetization of protons linked to PDMS chains is analysed to attempt to disclose the swelling mechanism of elementary chains.

5.1 GENERAL BEHAVIOUR. — The characteristic relaxation rate, δ , of the transverse magnetization was measured as a function of the number of solvent molecules per monomeric unit, n_s/n_m . Resulting curves corresponding to chloroform and heptane are shown in figures 8 and 9, respectively ; they all exhibit a typical shape characterized by a minimum of the relaxation rate, δ . The lower the concentration of

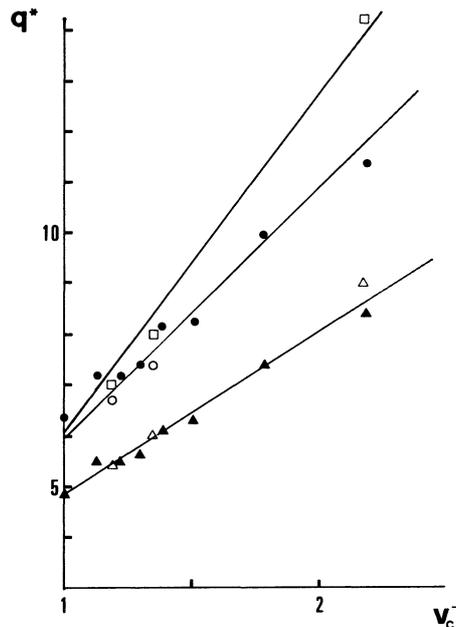


Fig. 6. — Swelling ratio q^* of PDMS gels observed at room temperature at equilibrium with good solvents ; v_c is the volume fraction of gel synthesis in toluene ; some data were obtained from reference [15], (\blacktriangle , \bullet) the swelling agents are : \blacktriangle , \triangle heptane ; \bullet , \circ toluene ; \square chloroform.

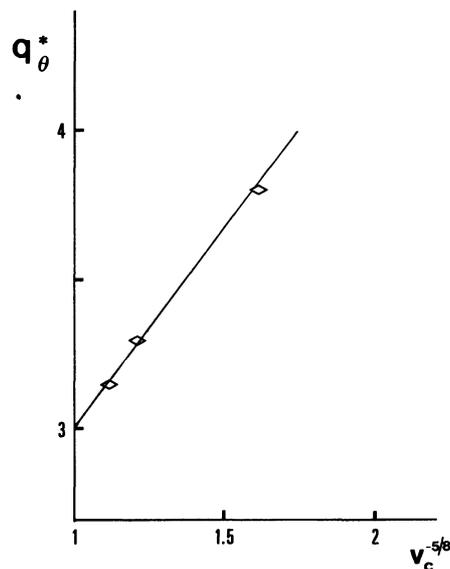


Fig. 7. — Swelling ratio q_θ^* of PDMS gels observed at 302 K at equilibrium with a theta-solvent (bromocyclohexane) ; the variable is $v_c^{-5/8}$.

synthesis of the gel and the lower the relaxation rate, measured at a given swelling ratio, q , determined by n_s/n_m .

5.2 INTERPRETATION.

5.2.1 The c^* -property. — Considering first the relaxation rate δ^* , measured at a maximum swelling ratio q^* , values of the product $q^* \delta^*$ are reported in

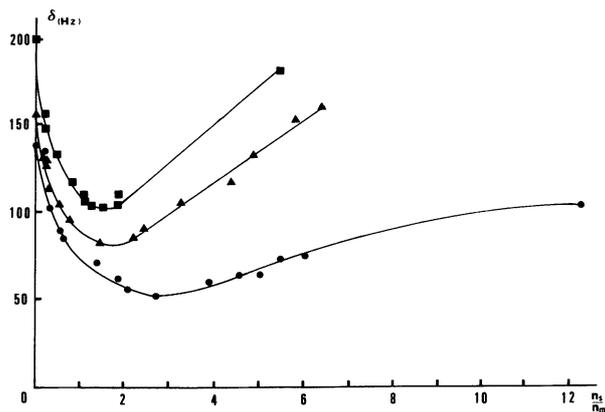


Fig. 8. — Variations of the transverse relaxation rate, δ , of protons linked to PDMS chains, observed on H9, H11 and H13 gels; \blacksquare H9; \blacktriangle H11; \bullet H13; the swelling agent is chloroform; the variable is the number of solvent molecules per monomeric unit.

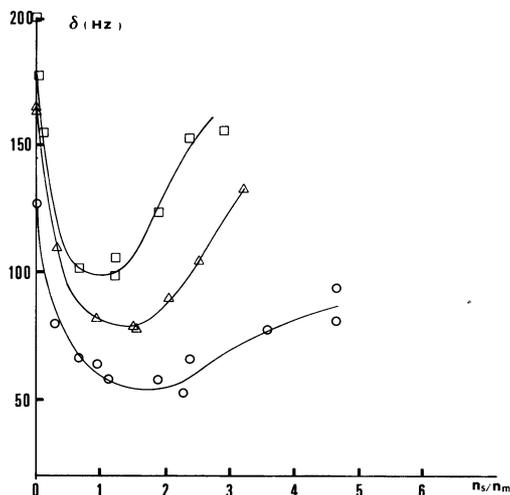


Fig. 9. — Variations of the relaxation rate, δ , observed on H9, H11 and H13 gels using heptane as a swelling agent.

table III. These values are found to hardly vary with the concentration of synthesis of the gels, in agreement with formula (11). This result is consistent with both the c^* -theorem proposed by de Gennes and also the key formula (3) where the end-to-end vector length $|\mathbf{r}_e|$ of an elementary chain is replaced with $(q^* N_e)^{1/3}$; the c^* -theorem permits to express the swelling ratio q^* as a function of the elementary chain contour length, N_e : $q^* \propto N_e^{4/5}$ [13].

5.2.2 *The packing condition.* — Considering now Log-Log plots of the relaxation rate, δ , as a function of the swelling ratio, q (Figs. 10a, b), the q_{II} range is found to exhibit linear variations; slopes of the straight lines are equal to 0.67 ± 0.05 , in accordance with formula (8) established by assuming that the spatial organization of elementary chains obeys a packing

Table III. — Values of the relaxation rate δ^* observed on gels at equilibrium with several solvents. Values of δ_d corresponding to the minimum value of the relaxation rate are also reported. Values of the products $q^* \delta^*$ on the one hand and $q_d^2 \delta_d$ on the other hand hardly vary with the volume fraction of synthesis v_c .

$M = 9\,700$	v_c	0.46	0.74	0.84	
	δ^* (Hz)	100	160	180	Chloroform
	$q^* \cdot \delta^*$	1 450	1 280	1 260	
	δ_d (Hz)	50	78	98	
	q_d	4.0	3.0	2.8	Bromo-cyclohexane
	$\delta_d \cdot q_d^2$	800	700	770	
	q_d^*	3.80	3.30	3.15	
	δ^* (Hz)	90	133	150	Heptane
	$q^* \delta^*$	1 080	994	1 000	
	δ_d (Hz)	50	73	94	
	q_d	4.2	3.3	3.0	
	$\delta_d \cdot q_d^2$	880	795	846	

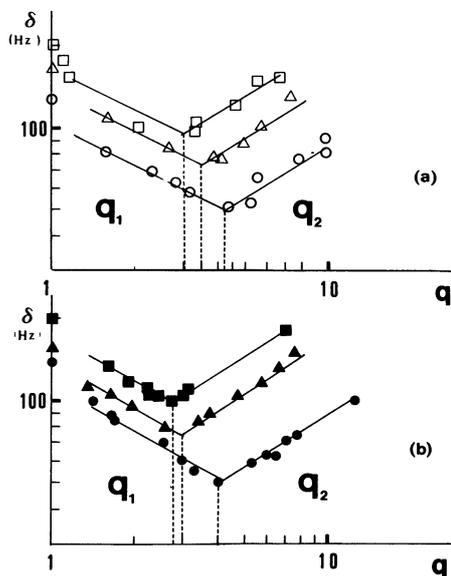


Fig. 10. — Log-Log plot of variations of the transverse relaxation rate, δ , as a function of the swelling ratio q ; the swelling agent is: (a) chloroform; (b) heptane.

condition: the average end-to-end vector length $|\mathbf{r}_e|$ of an elementary chain is replaced by $(qN_e)^{1/3}$ at any q value within the q_{II} range.

5.2.3 *A superposition property.* — The concentration of synthesis, v_c , is now taken into consideration in

the analysis of results of the q_{II} swelling ratio range, by using the reduced variable $q^{2/3} v_c^{5/3}$ in accordance with formula (12). All curves represented on figures 8 and 9 can be brought into reasonable coincidence as is shown on figure 11. We consider that this figure demonstrates the existence of a superposition property of relaxation rates, δ , within the uncertainty of NMR measurements. This result is consistent with both the N_e^{-2} dependence of the key formula (3) and the determination of the elementary chain mean contour length $N_e(v_c)$ from the screening effect observed in semi-dilute solution : $N_e \propto v_c^{-5/4}$.

5.2.4 Elementary Gaussian chains : a packing condition. — We are now left with the analysis of the q_I swelling ratio range. The crucial point of the interpretation is to assume that the key formula (3) which was shown to reasonably apply to the interpretation of δ variations in the q_{II} swelling ratio range also applies within the q_I range. The interpretation of the swelling degree value q_d corresponding to the minimum of the relaxation δ , is first considered (Figs. 8 and 9); q_d is determined in an easy way by using Log-Log plots (Figs. 10a and b). Values of q_d are reported in table III; they are compared with those of the swelling ratio q_0^* measured on a gel at equilibrium with a theta-solvent. We consider that q_0^* and q_d values are in reasonable agreement with one another. We now assume that q_d reflects a packing condition applied to the spacial organization of Gaussian elementary chains. Accordingly, q_d is expressed as :

$$q_d \propto N_e^{1/2} \tag{18}$$

and, from formula (3), the minimum relaxation rate δ_d should be written as :

$$\delta_d \propto q_d^{2/3} / N_e^{4/3} = q_d^{-2} . \tag{19}$$

Values of the product $\delta_d q_d^2$ are reported in table III; they may be considered as a constant for a given polymer-solvent system.

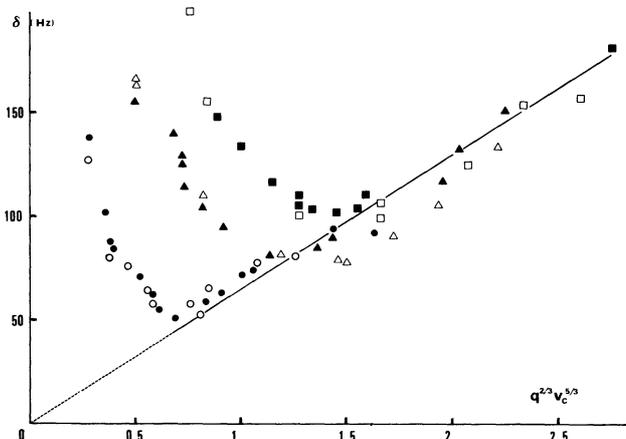


Fig. 11. — Variations of the transverse relaxation rate, δ , are plotted as a function of the reduced variable $q^{2/3} v_c^{5/3}$; they correspond to curves drawn on figures 8 and 9.

Furthermore, the swelling ratio $q_d \propto N_e^{1/2}$ may be expressed as a function of the concentration of synthesis v_c of the gel, as :

$$q_d \propto v_c^{-5/8}; \tag{20}$$

variations of q_d as a function of the variable $v_c^{-5/8}$ are reported on figure 12; a linear dependence is observed.

Finally, measurements of q^* and q_d could be applied to the investigation of some polymeric gel properties in the following way. Assuming that the packing condition applies in the same way to fully swollen elementary chains and to Gaussian ones (geometrical factors, α , involved in the swelling process have the same value) q^* is written as :

$$q^* \propto x^* N_e^{3v-1} v_p^{3(2v-1)} \tag{21}$$

v_p is the excluded volume parameter; while :

$$q_d \propto x_d N_e^{0.5}$$

with $v=0.588$ and $x^* = 8 \pi (a_0^2 C_\infty / 7)^{3/2} \alpha \rho_p \mathcal{A} / 3 M_p$; $a_0 = 1.6 \text{ \AA}$, is the mean length of the main chain bond; $C_\infty = 7.0$ is the characteristic ratio of PDMS chains; ρ_p is the pure polymer density; M_p is the molar weight of one monomeric unit and \mathcal{A} is the Avogadro number; $x_d = 8 \pi (a_0 C_\infty / 6)^{3/2} \alpha \rho_p \mathcal{A} / 3 M_p$; therefore, the elementary chain contour length is eliminated from the ratio $(q^*)^{1/6v-2} / q_d$; corresponding values are reported in table IV; they may be considered as independent of the concentration of synthesis of a gel for a given solvent. The value 1.2 of this ratio for the PDMS-heptane system leads to an estimate of $v_p = 0.9 \alpha$. The total thermodynamic interaction characterizing the PDMS-heptane system has been estimated by Flory : $v_1 = 0.2$ at 298 K [1]; therefore, the geometrical factor α is about equal to 0.22.

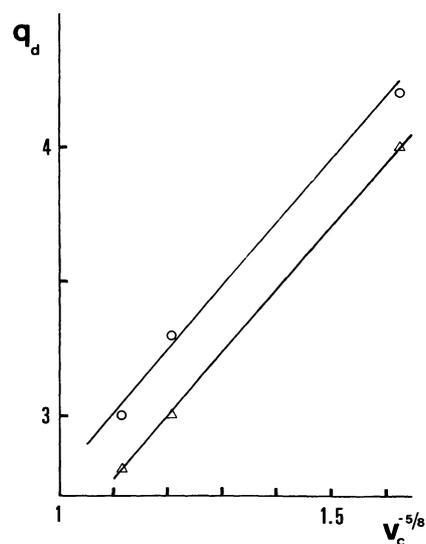


Fig. 12. — Variations of the swelling ratio q_d corresponding to the minimum value of δ are drawn as a function of $v_c^{-5/8}$; v_c is the synthesis concentration of the gel.

Table IV. — Values of the ratio $(q^*)^{0.654}/q_d$ calculated to eliminate effective chain length effects.

	Solvent	V_c	0.46	0.74	0.84
$(q^*)^{0.654}/q_d$	Chloroform		1.4	1.3	1.3
	Heptane		1.2	1.1	1.2

We consider that NMR measurements performed on PDMS polymeric gels might be a simple approach to the determination of the relative strength of thermodynamic interaction parameters characterizing several polymer-solvent systems and to the investigation of the rôle of the number of functional crosslinkages in elementary chain swelling processes.

5.2.5 Chain desinterspersion : a superposition property. — Considering that the q_d swelling ratio corresponds to a packing condition applied to the spatial organization of Gaussian elementary chains, it is now assumed that the q_1 swelling ratio range reflects the desinterspersion of elementary chains; in a dry polymeric gel all chains are swollen by one another; then, a progressive desinterspersion is supposed to occur; it is induced by solvent molecules replacing monomeric units [25]. The desinterspersion process is achieved when the swelling ratio value q_d is reached. In the q_1 range, the quantity δ/v_c was found to obey an empirical superposition property using the reduced variable $qv_c^{5/8}$; all curves drawn on figures 8 and 9 are brought into reasonable coincidence on figure 13. The dependence of δ upon q is found to be about $\delta \propto q^{-0.6}$. More measurements would be necessary to give a detailed description of properties of elementary chains in this q_1 swelling ratio range. However, a qualitative analysis is proposed in this paper; it is based on a submolecule concept. It is worth noting first that the submolecule concept associated with

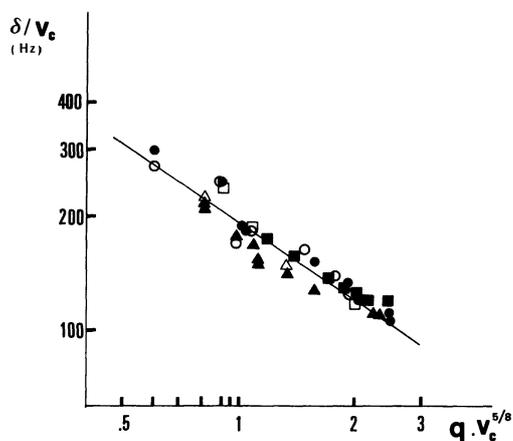


Fig. 13. — A superposition property of the quantity δ/v_c is observed as a function of the reduced variable $qv_c^{5/8}$ (q_1 swelling ratio range).

hydrodynamic screening effects has already been applied to the description of NMR properties observed on strongly entangled long chains [9, 26]. A superposition property induced by polymer concentration variations was shown to characterize the spin-system response at any time. This superposition property is consistent with both formula (6) and the usual concentration dependence of the submolecule contour length $N_e \propto c^{-1}$. Such a property extended to polymeric gels would lead to a q^{-1} dependence of δ ; this dependence is in disagreement with the experimental results.

Nevertheless, it is easily seen that the submolecule concept still applies to polymeric gels because of the order of magnitude of relaxation rates δ ($\approx 10^2$ Hz) measured on polymeric gels; this order of magnitude indicates that a strong reduction of spin-spin interactions is induced by the local motion of monomeric units (formula (6)) and also that the motional averaging process is only partial, reflecting some topological constraints; otherwise δ should be close to 1.0 Hz.

It is believed that in the q_1 swelling ratio range :

- i) there is an effective mesh size of the network different from that induced by the concentration of trapped topological constraints corresponding to the synthesis concentration of the gel;
- ii) the mesh size is slowly increased by adding small amounts of solvent to the gel;
- iii) the mesh size corresponding to trapped topological constraints is obtained when the q_d value is reached.

Furthermore, we consider that the presence of covalent crosslinks may strongly modify the probability distribution function of submolecule end-to-end vectors \mathbf{r}_e ; both its mathematical structure and the q dependence of its width associated with a correlation length $\xi_{N_e}(q)$ may change the resulting observed average value of δ . This problem will be discussed in a subsequent paper.

5.3 CONCLUDING DISCUSSION. — The main feature perceived from the interpretation of NMR properties observed on progressively swollen polymeric gels is the two-step swelling process of elementary chains. This two-step mechanism is contrasted to the progressive disentanglement phenomenon induced by chain dilution going from concentrated solutions to semi-dilute ones. In the latter case, concentrated solutions are characterized by a screening length ξ_g , which depends upon the polymer concentration, c , as a c^{-1} function; the number of monomeric units n_g involved in the corresponding contour length is $n_g \propto c^{-2}$; while semi-dilute solutions are characterized by a screening length ξ_s which depends upon the concentration as a $c^{-3/4}$ function; the corresponding number of monomeric units is $n_s \propto c^{-5/4}$. A cross-over is predicted to occur when $\xi_g \approx \xi_s$ whereas, in polymeric gels, NMR properties show that

the effective mesh size of the network increases upon solvent addition until the contour length of a sub-molecule is equal to the elementary chain length. Then, by adding more solvent, elementary chain properties go from a Gaussian behaviour to that induced by an excluded volume effect; this latter one was already predicted by de Gennes.

Therefore, neither the usual static screening effect nor the usual hydrodynamic screening property apply in a simple way to the description of polymeric gels; the screening is modified by the presence of permanent crosslinks.

Furthermore, it must be noted that NMR properties are described without taking fast fluctuations of end points of elementary chains into consideration.

6. Conclusion.

The purpose of the present paper was to show that the progressive swelling of elementary chains in a gel can be conveniently monitored from the strength of a non-zero average of tensorial spin-spin interactions; this average reflects an orientational order of monomeric units induced by topological constraints exerted on chains; it corresponds to a transfer of localization of NMR properties from a local space-scale to a semi-local one.

The deviation of monomeric motions from isotropic diffusional rotations is a small effect; however, it is easily observed from NMR high resolution spectroscopy. From the present NMR study, it is suggested to describe the progressive swelling of elementary chains as a two-step process (Fig. 14). Starting from a dry gel, the desinterspersion of chains occurs in the first step; elementary chains have Gaussian properties until the swelling ratio q_d is reached; then, excluded volume effects progressively arise in the second step; this step is also characterized by a spatial organization of chains obeying a packing condition (Fig. 14). It is like considering that the transition from Gaussian properties to excluded volume effects is a smooth onset.

These two steps are perceived although the macroscopic gel swelling obeys a simple addition law of volumes of solvent and polymer.

The present NMR study also shows that trapped

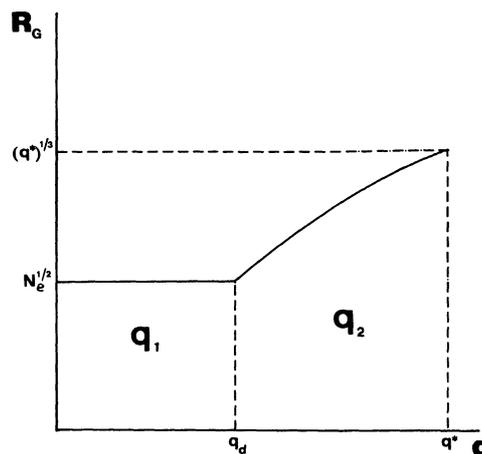


Fig. 14. — A schematic behaviour of the radius of gyration of elementary chains is proposed from the NMR study.

topological constraints act as covalent crosslinks; they determine a cut in correlations of space fluctuations of elementary chains; this interpretation was already proposed in reference [15].

Finally, the transverse magnetic relaxation rates of protons linked to elementary chains were shown to exhibit several superposition properties induced by swelling ratio variations or by changing the concentration of synthesis of the gel. These superposition properties strongly reinforce the proposed description of the swelling mechanism of elementary chains; they also prove that the basic formula used to calculate the transfer of localization of NMR properties from a local space-scale to a semi-local one is in satisfactory agreement with experimental results.

We consider that the relaxation of the transverse magnetization is a tool well appropriate to semi-local investigations of properties of polymer systems; it has been already shown that it conveniently reflects the disentanglement process of long chains in concentrated solutions [26, 27].

Acknowledgments.

The authors wish to acknowledge the support of this work by the D.R.E.T. (Grant n° 82/1057).

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